THE EFFECTS OF HIGH TEMPERATURE ANNEALING AND COMPOSITION ON THE DIELECTRIC PROPERTIES OF THIN FILMS OF $Ba_xSr_zTiO_3$

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ABSTRACT

Single phase, (100) oriented $Ba_{0.5}Sr_{0.5}TiO_3$ films have been deposited by pulsed laser deposition onto (100) $LaAlO_3$, $SrTiO_3$, MgO substrates. The dielectric properties of these films were measured using interdigitated capacitors as a function of DC bias and temperature at 1 MHz and as a function of DC bias at 1 to 20 GHz at room temperature. Deposited films were annealed over a temperature range of 900 to 1350 C for 1 to 8 hours to observe its effect on dielectric properties. Chemical analysis on films deposited from stoichiometric targets showed the films to be up to 6% deficient in Ba and Sr under typical PLD deposition conditions. Optimal annealing conditions and target stoichiometries for minimizing dielectric loss and maximizing tuning are discussed.

INTRODUCTION

Ferroelectric (FE) thin films grown by pulsed laser deposition (PLD) are currently being explored as the dielectric medium in tunable capacitors for the development of a low phase noise voltage controlled oscillator (VCO) to operate in the 1.5 to 2.5 GHz range. The device is to be based on the large electric field dependence of the dielectric constant in FE materials near their ferroelectric-paraelectric (FE/PE) phase transition [1]. This effect has already been demonstrated in FE films deposited by PLD [2]. The critical issues that need to be addressed for the FE VCO are percent tuning and dielectric loss.

The solid solution $Ba_xSr_{1-x}TiO_3$ (BST) is well suited for the development of FE based microwave electronics. The Curie temperature of BST ranges from 0 K to 400 K for x = 0 to 1 [3]. Being able to control the phase transition temperature in such a simple way is important because the electric field dependence of the dielectric constant is largest at the phase transition. However, it is necessary to remain just to the paraelectric side of the phase transition of the material to eliminate the losses due to ferroelectric domain wall motion in the ferroelectric phase [4].

We have grown BST thin films by PLD and investigated their structure, morphology and dielectric properties for a variety of annealing conditions. The chemical composition of the PLD targets was also modified to observe the effects on dielectric the properties.

EXPERIMENTAL

The FE films were deposited directly onto single crystal (100) $SrTiO_3$ (STO), MgO and $LaAlO_3$ (LAO) substrates by PLD. The output of a short pulsed (30 ns FWHM) excimer laser operating with KrF (248 nm) at 5 Hz was focused to a spot size of ~ 0.1 cm^2 and an energy density of ~1.9 J/cm^2 onto the desired targets. Films were deposited with a substrate-target distance of 3.5 -5.5 cm, O_2 pressure of 0.35 Torr, and substrate temperature of 700° - 800° C.

The primary constituents of the targets were equal molar amounts of $BaTiO_3$ and $SrTiO_3$. Barium oxide or SrO was added if excess Ba or Sr was desired in the target. The desired powders were then mixed in a mechanical shaker for 30 minutes and pressed into the form of a pellet 1 inch in diameter under 2000 lbs for 15 minutes. The pressed pellets were then dried and calcined in Pt foil at 800° C for 4 hours, crushed, repressed and sintered in Pt foil at 1350° C for 6 hours.

Chemical analysis of the films was performed by inductively coupled plasma spectroscopy (ICP) (Galbraith Labs) and electron-beam microprobe analysis to determine the elemental ratios of Ba, Sr and Ti. The films used for ICP were grown in the perovskite phase on (100) yttrium barium copper oxide (YBCO) on a (100) MgO substrate. The BST films were then removed from the MgO by immersing the sample in 10% HCl, where the YBCO is dissolved leaving a free standing BST film which was then rinsed with distilled H_2O and methanol before shipping for elemental analysis.

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BST films that were post-deposition annealed at temperatures below 1050° C were done in flowing O_2. Films annealed above 1050° C were done in a BST vessel that was wrapped in platinum foil (Figure 1) and place in an alumina tube that was capped at both ends, flushed with O_2 before annealing and maintained at a slight positive pressure of O_2 during the annealing process.

Interdigitated capacitors were deposited on top of the FE films through a PMMA lift off mask by e-beam evaporation of 1-2 μm thick Ag and a protective thin layer of Au. Interdigitated capacitors had finger lengths of 10 to 100 μm with gaps that ranged from 5 to 15 μm. One to twenty GHz microwave measurements were made on an HP 8753 network analyzer at room temperature. Temperature dependent measurements were performed at 1 MHz using a HP 4285A Precision LCR Meter. All films were characterized by x-ray diffraction (XRD) and representative films were coated with 500 Å of Au/Pt for scanning electron microscopy (SEM).

RESULTS

Chemical Analysis

The atomic ratios found from elemental analysis were scaled to give Ti the value of one. The data suggest there is approximately a 6 % deficiency in Ba and Sr from their anticipated stiochiometric ratios (Table I). These deficiencies were not affected by changing the deposition temperature from 700°c to 800° C, or the substrate target distance from 3.5 cm to 5.5 cm, or by compensating the PLD target with up to 11.8 % excess Ba and 3.6 % excess Sr.

X-Ray Diffraction

All as-deposited BST films grown on oxide substrates were found to be single phase and exclusively oriented in the (100) direction (Figure 2 a)). Typical FWHM of the ω-scan peaks of the films on (100) MgO were 0.6 to 0.9°, and at or below the 0.166° resolution limit of the diffractometer for BST films on (100) STO or LAO. Films were annealed to improve dielectric properties, however x-ray diffraction shows that interdiffusion of the substrate and film can occur. Figure 2 b) shows the x-ray diffraction pattern of a film before and after being annealed at 1350° C for 6 hours. The (200) BST diffraction peak of the film shifts towards the (200) diffraction peak of the STO substrate as the Sr from the substrate and the Ba from the film interdiffuse.

Effects of Annealing on Film Morphology

As-deposited BST films show mirror like smoothness to the eye but have a grain size of ~250 Å as observed by SEM (Figure 3 a)). After annealing at 900° C for 8 hours, the films were smoother but the surface topology still suggests grain boundaries underneath (Figure 3 b)). Annealing at temperatures above 1000° C in flowing O_2 resulted in surface coarsening such that the films could no longer be patterned for devices. The films became cloudy to the eye and showed what appeared to be erosion at the grain boundaries, revealing a 20 fold increase in grain size from the as deposited films (Figure 3 c)). Using a "bomb" to increase the partial pressure of the films elements in the vapor surrounding the film completely stopped the grooving around the grains and allowed annealing temperatures of 1250° C while the films maintained a smooth surface that revealed no grain boundaries (Figure 3 d). The effectiveness of bomb annealing was diminished at temperatures above 1275° C, were surface coarsening became evident again.

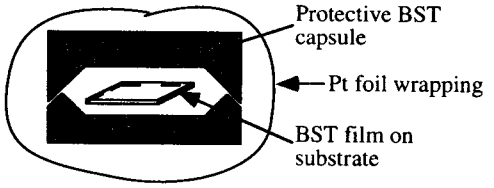

FIGURE 1 Schematic diagram showing the arrangement used during annealing of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) films. Both the Pt foil and the BST vessel are there to help create an equilibrium vapor pressure of Ba, Sr, Ti, and O in the immediate vicinity of the BST film.

Table I The atomic ratios of Ba, Sr and Ti as measured by electron-beam microprobe analysis and inductively coupled plasma spectroscopy were scaled to give Ti the value of one.

Analysis Technique	Ba (atomic ratio)	Sr (atomic ratio)	Ti (atomic ratio)
Theoretical Bulk	0.500	0.500	1.000
Electron-beam Microprobe	0.478 ±0.020	0.467 ±0.020	1.000 (normalized)
ICP (Galbraith Labs)	0.478 ±0.020	0.456 ±0.020	1.000 (normalized)

Dielectric Measurements

Dielectric measurements at 1 MHz were made as a function of temperature and DC bias field. Figure 4 shows the capacitance and dissipation curves of interdigitated capacitors with 5 μm gaps at 0, 20, and 40 V DC bias for five films that differ mostly by their annealing conditions. Figure 4 a) and b) were measurements made from $Ba_{0.35}Sr_{0.65}TiO_3$ films deposited on (100) LAO where the films were measured as deposited and after annealing at 900° C in O_2 for 8 hours, respectively. Figures 4 c) and d) are a measurement made from a $Ba_{0.5}Sr_{0.5}TiO_3$ film on (100) STO that has been annealed in a BST bomb at 1250° C for 2 hours. Figures 4 e) and f) were made from $Ba_{0.5}Sr_{0.5}TiO_3$ films on (100) STO that were annealed in a BST bomb for 6 hours at 1275° C and 1300° C respectively. All films show features in the capacitance or dissipation factor at ~50 K, which may correspond to the bulk BST tetragonal-orthorhombic phase transition or the effect of the STO substrates increase in dielectric constant at lower temperatures for films on STO. The peaks at ~250 K correspond to the bulk FE/PE (cubic-tetragonal) phase transition. The important features to notice in Figures 4 a) - c), are that at as the annealing temperatures reach 1250° C the capacitance and dissipation peaks that correspond to the FE/PE phase transition become sharper and the peaks in dissipation shift to lower temperature as compared to their respective peaks in capacitance. The approximate half maximum peak widths of the capacitance versus temperature were 150 K, 120 K, and 90 K for the as deposited, annealed at 900° C, and annealed at 1250° C films, respectively. Likewise, the peak in dissipation shifted from ~50 K above the peak in capacitance for the as deposited film, to ~50 K below capacitance for the film annealed at 1250° C. In bulk BST, the peak in capacitance versus temperature is much sharper (FWHM ~ 25 K) than in the films [5]. Also, in bulk material the dissipation is always lower in temperature than the peak in capacitance, that is in the ferroelectric phase. As deposited films do not behave like bulk material in these regards and only after annealing do bulk-like properties begin to recover.

The films can be over annealed, as shown in Figures 4 d) - f). Figure 4 d) is the same as Figure 4 c) and is placed there to make comparisons with Figures 4 e) and f) easier. At annealing temperatures above 1250° C, the peak in capacitance begins to broaden and increase its overlap with the dissipation peak. The approximate peak widths in capacitance are 90 K, 100 K, and

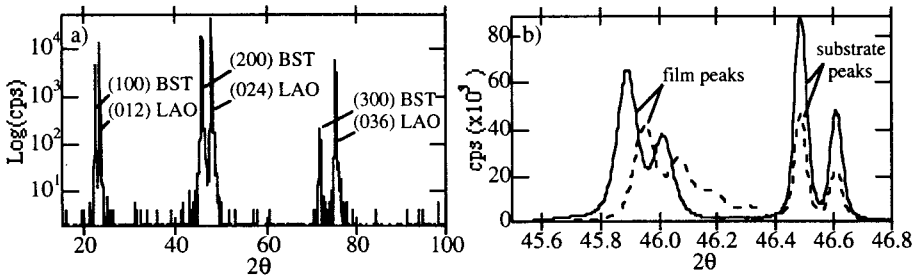

FIGURE 2 Theta/two-theta x-ray diffraction pattern of a a) 0.5 μm $Ba_{0.5}Sr_{0.5}TiO_3$ on (100) $LaAlO_3$, and b) 7 μm of $Ba_{0.5}Sr_{0.5}TiO_3$ on (100) $SrTiO_3$ as deposited (solid line) and after annealing (dashed line) in an encapsulated environment at 1350° C for 6 hours.

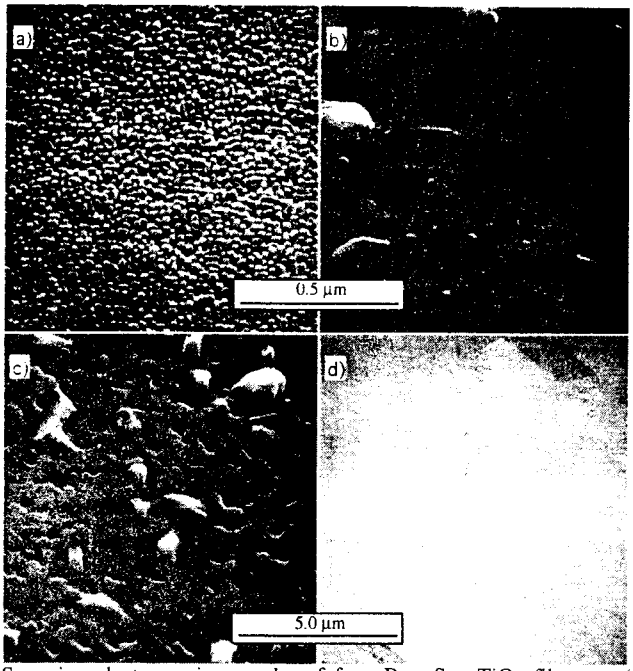

FIGURE 3 Scanning electron micrographs of four $Ba_{0.5}Sr_{0.5}TiO_3$ films on (100) $LaAlO_3$ annealed under different conditions. a) As deposited, b) annealed at 900° C for 8 hours in flowing O_2, c) annealed at 1140° C for 12 hours in flowing O_2 and d) annealed at 1250° C for 12 hours in an environment enclosed by $Ba_{0.5}Sr_{0.5}TiO_3$ in O_2.

150 K for the 1250° C, 1275° C and 1300° C annealed films respectively. Increases in overlap of the peaks diminishes the use of the films for high tuning, low loss microwave devices.

Dielectric measurements made between 1 and 20 GHz at room temperature for a representative set of samples are shown in Table II. The range of the quantity Q given is the reciprocal of the dielectric loss over the bias range, and the percent tuning is the change in capacitance over the bias voltage range divided by the zero bias capacitance. Using percent tuning times average Q as a figure of merit that maximizes film properties for making low loss tunable capacitors, it is clear that adding 2 % excess Ba and Sr to the PLD targets and annealing the films improves the film properties. Further studies of BST on MgO, LAO and STO substrates in the 1 to 20 GHz range indicated that compensating the targets with more than 2 % excess Ba and Sr only diminish film properties. Optimal bomb annealing conditions for the films were 1125° C for 2 hours for BST on LAO or MgO, and 1250 ° C for 2 hours for BST on STO. Higher temperatures or longer durations either did not improve or diminished film properties.

DISCUSSION

From the data presented here, there is a strong relationship between annealing temperature, grain size and dielectric properties. This has been seen previously in bulk BST and has been reproduced in these films [5]. SEM showed as-deposited films to have small grain size (~250 Å) while capacitance measurements showed dielectric properties very different from the large grained and single crystal FE material [5,6]. Temperature dependent measurements of the as deposited film showed broad peaks in the capacitance and dissipation factor as a function of temperature. Large tuning in this film was only observed at temperatures where the dielectric loss was high. As films

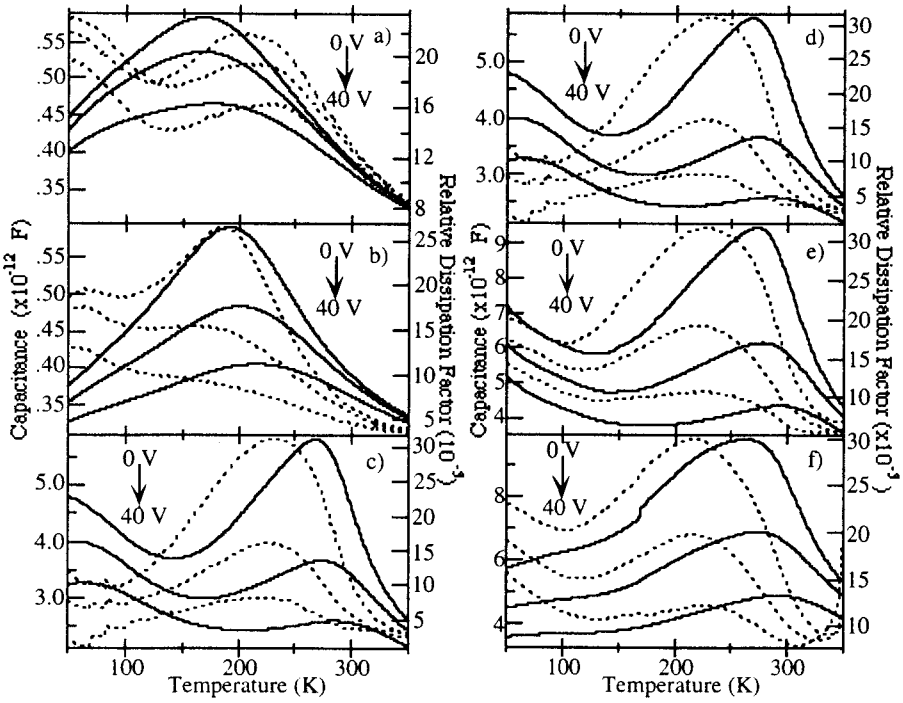

FIGURE 4 Capacitance (solid) and dissipation (dashed) measurements made at 1 MHz with 5 μm gap interdigitated capacitors at 0, 20, and 40 V DC bias as a function of temperature. a) and b) are 0.5 μm thick $Ba_{0.35}Sr_{0.65}TiO_3$ on (100) $LaAlO_3$, as deposited and annealed at 900° C in O_2 for 8 hours, respectively. The other films are 7 μm thick $Ba_{0.5}Sr_{0.5}TiO_3$ on (100) $SrTiO_3$ annealed in a $Ba_{0.5}Sr_{0.5}TiO_3$ capsule in O_2. The sample for c) and d) was annealed at 1250° C for 2 hours and the graphs are the same graph placed twice for easy comparison of the data. The sample for e) was annealed at 1275° C for 6 hours, and f) 1300° C for 6 hours.

were annealed in O_2, the grain size increased and bulk-like dielectric properties began to emerge. The capacitance and dissipation curves as a function of temperature sharpened, and the peak in dissipation shifted to below the peak in capacitance, as in bulk FE materials.

TABLE II 0.5 μm gap interdigitated capacitor properties at 10 GHz at room temperature. Samples that demonstrated median properties for its fabrication conditions were chosen. Percent tuning times average Q over the bias range selected is used as a figure of merit that maximizes film properties necessary for device fabrication.

$Ba_{0.5}Sr_{0.5}TiO_3$ films on (100) MgO sample description	Q (0-40V bias)	C (pF) (0-40V bias)	% Tuning (0-40V bias)	% Tuning x Avg. Q
0.5 μm thick, 1000° C annealed PLD target was stoichiometric BST	6 - 19	0.97 - 0.43	56 %	7.0
0.5 μm thick, 1000° C annealed, PLD target had 2% extra Ba and Sr	19 - 42	0.84 - 0.54	36 %	11.0
0.5 μm thick, 1125° C annealed PLD target had 2% extra Ba and Sr	13 - 37	0.44 - 0.22	49 %	12.3

Despite the recovery of some of the bulk behavior by annealing at the optimal temperature and duration, the capacitance peak widths for the films (FWHM ~ 100 K) are still much broader than in the bulk (FWHM ~ 25). The broadening of the capacitance peaks versus temperature in the films is due to a broadening of the temperature dependence of the FE/PE phase transition. It is speculated that the phase transition broadening is both homogeneous and inhomogeneous. Possible homogeneous effects would be those that might "frustrate" each grain equally, such as grain boundary effects, finite grain size effects, and nonstoichiometry. Inhomogeneous effects would cause different grains to go through the phase transition at different temperatures and these effects might include strain due to lattice mismatch at the substrate, strain due to neighboring particles, grain size effects on a distribution of grain sizes or a non-uniform contamination of the film by elements in the substrate.

Annealing affects all of these possible sources of phase transition broadening. Annealing sharpens the phase transition by reducing film strain, decreasing oxygen deficiencies, and promoting grain growth which reduces grain size and grain boundary effects. However, interdiffusion of elements in the film and the substrate become important at higher annealing temperatures and broadens the measured phase transition of the film.

Film stoichiometry also has a strong effect on dielectric properties. Chemical analysis shows the films to be ~6% deficient in Ba and Sr. Increasing the amount of available Ba and Sr in the target by 2 % does not give a measurable increase of Ba and Sr in the films, but it does result in ~ 60% improvement in film properties for making low loss tunable capacitors. It is suggested that the stoichiometry may have a fixed deficiency in Ba and Sr due to surface effects at grain boundaries. As deposited, each grain is a tall columnar structure approximately 125 Å in radius. Each unit cell is approximately 4 Å in size, giving and inner core of 121 Å and a 4 Å surface layer that represents 7 % of the total volume. If the surface of each grain is passivated by a monolayer of TiO_x, this would account entirely for the Ba and Sr deficiency.

The volatility of the elements in the films being annealed becomes important at temperatures above 1000° C. The vapor pressure of the elements in BST are low, but surface smoothness is crucial for device patterning, thus annealing in an encapsulate environment can become necessary.

CONCLUSION

High quality single phase (100) oriented BST films were grown by PLD. Film morphology and structure were characterized by SEM and XRD. Dielectric properties were measured from 1 - 20 GHz at room temperature and at 1 MHz as a function of temperature. These measurements showed that the dielectric properties could be significantly improved by annealing under the appropriate conditions. Chemical stoichiometry was also shown to have a profound effect on dielectric properties. Precautions needed to be taken to avoid the volatilization of elements in the films when annealed at temperatures above 1000° C.

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